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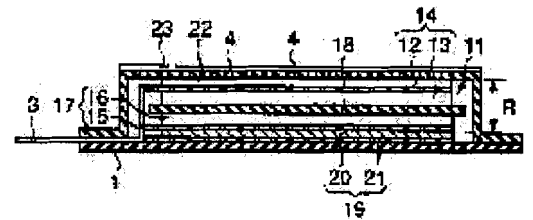
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(54) NONAQUEOUS ELECTROLYTE CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte cell with improved capacity.

SOLUTION: The nonaqueous electrolyte cell comprises a positive electrode 14; a negative electrode 17 facing the positive electrode 14; a nonaqueous electrolyte containing layer interposed between the positive electrode 14 and the negative electrode 17; and a case 1 housing the positive electrode 14, the negative electrode 17, and the nonaqueous electrolyte containing layer, to which, a plurality of vent holes 4 for supplying oxygen to the positive electrode 14 are opened. A lithium storing body 19, having a lithium storing layer 20 making the negative electrode 17 store lithium ion by releasing lithium ion at the potential baser than that of the negative electrode 17, is housed in the case 1 so as to fulfill the formula; $0.25P \leq R \leq 0.98Q$, where, R represent the distance between the vent holes and the surface of the lithium storing layer, P represents the distance between the inner surface of the case on which the vent holes are formed, and an inner surface of the case facing the above inner surface, or 1/2 of the distance between two surfaces of the case facing each other on which, vent holes are formed, Q represents a shortest distance out of respective distances to the farthest part of the inside surface of the case at respective vent holes.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a nonaqueous electrolyte battery, and relates to the nonaqueous electrolyte battery which uses oxygen as positive active material especially.

[0002]

[Description of the Prior Art]In recent years, a power supply has also come to be asked for it being small and lightweight as the commercial scene of portable information machines and equipment, such as a cellular phone and an electronic mail terminal, is expanded quickly and the small weight saving of these apparatus follows it. Although the rechargeable lithium-ion battery which is high energy density is used abundantly now at these portable devices, the rechargeable battery with which high capacity is obtained further is called for.

[0003]Since the air cell which uses oxygen in the air for positive active material does not need to contain positive active material in a cell, it can expect high capacity-ization. The air lithium secondary battery which has the composition which is explained below as a lithium secondary battery which uses metal lithium for negative electrode active material, and uses oxygen for positive active material is known.

[0004]This air lithium secondary battery possesses the four-layer laminated material which comprised a polymer electrolyte film which intervenes between an anode, a negative electrode, and said anode and said negative electrode, and an oxygen transmission film laminated on said anode. This four-layer laminated material is enclosed with lamination bag manufacture. The anode made the catalyst bed which consists of acetylene black containing cobalt, and the polymer electrolyte film which consists of polyacrylic nitril, ethylene carbonate, propylene carbonate, and LiPF_6 stick to a nickel network or an aluminum network by pressure. On the other hand, the negative electrode is formed from lithium foil.

[0005]However, since such an air lithium secondary battery is using metal lithium for a negative electrode, if a charging and discharging cycle is repeated, a dendrite will generate it on the metal lithium surface. If the generated dendrite is missing, it will lead to capacity lowering and it will grow, and it has a possibility of connecting too hastily if an anode is contacted.

[0006]In order to compensate this fault, the air rechargeable lithium-ion battery which uses a carbon material for a negative electrode is proposed (JP,10-83836,A publication before examination). A carbon material has occlusion and the capability to emit reversibly in a lithium ion, and improvement in a cycle characteristic of it is

attained as compared with the air lithium secondary battery which used metal lithium for the negative electrode.

[0007]In the JP, 10-83836, A publication before examination, lithium oxide like a lithium peroxide (Li_2O_2) is added to the anode containing carbonaceous material and a conducting agent, and this lithium oxide is used as a lithium source.

[0008]It is necessary to charge before use in the rechargeable lithium-ion battery indicated to this JP, 10-83836, A publication before examination. However, since some lithium oxide will be omitted from an anode by emitting lithium from lithium oxide of the portion in contact with a conducting agent if the anode containing lithium oxide is charged, there is a problem that high capacity cannot be obtained.

[0009]

[Problem(s) to be Solved by the Invention]An object of this invention is to provide the nonaqueous electrolyte battery whose capacity improved.

[0010]

[Means for Solving the Problem]A negative electrode in which a nonaqueous electrolyte battery concerning this invention counters with an anode and said anode, In a nonaqueous electrolyte battery possessing a container with which the opening of the vent for storing a nonaqueous electrolyte contained layer arranged between said anode and said negative electrode, and said anode, said negative electrode and said nonaqueous electrolyte contained layer, and supplying oxygen to said anode is carried out, It is stored in said container so that lithium storage bodies provided with a lithium storage reservoir which emits a lithium ion with **** potential and carries out occlusion of the lithium ion to said negative electrode rather than said negative electrode may satisfy following the (1) type.

[0011]

$0.25P \leq R \leq 0.98Q$ (1)

However, said R is shown and distance from said vent to said lithium storage reservoir surface said P, It is the distance of an inner surface of said container with which said vent was formed when said vent was formed in the whole surface of said container, this inner surface, and a container internal surface that counters, Expressing one half of sizes of said two face-to-face distance, when said vent is formed in two fields where said container counters mutually, said Q is the shortest distance among each distance to the furthest part of an inner surface of said said container about the vents of each.

[0012]

[Embodiment of the Invention]Hereafter, an example of the nonaqueous electrolyte battery (the case of the both sides of a primary battery and a rechargeable battery is included by the nonaqueous electrolyte battery here) concerning this invention is explained.

[0013]This nonaqueous electrolyte battery is provided with the following.

The electrode group containing the nonaqueous electrolyte contained layer arranged between an anode, a negative electrode, said anode, and said negative electrode.

The container with which two or more openings of the vent for said electrode group being stored and supplying oxygen to said anode are carried out.

It is stored so that lithium storage bodies provided with the lithium storage reservoir which emits a lithium ion

with **** potential and carries out occlusion of the lithium ion to said negative electrode rather than said negative electrode may satisfy following the (1) type in this container.

[0014]

$$0.25P \leq R \leq 0.98Q \quad (1)$$

However, said R is shown and the distance from said vent to said lithium storage reservoir surface said P, In the distance of the inner surface of said container with which said vent was formed when said vent was formed in the whole surface of said container, this inner surface, and the container internal surface that counters. Expressing one half of the sizes of said two face-to-face distance, when said vent is formed in two fields where said container counters mutually, said Q is the shortest distance among each distance to the furthest part of the inner surface of said container about said each of vent.

[0015]The lithium storage reservoir surface does not show the occupancy surface of a lithium storage reservoir. For example, as shown in drawing 10 mentioned later, when the opening of the hole is carried out to the lithium storage reservoir, R does not mean the distance of the opening part (occupancy surface) and the vent 4, and sets distance of the surface and the vent nearest to a vent to R among the lithium storage reservoirs which actually exist.

[0016]In this nonaqueous electrolyte secondary battery, it can have an oxygen diffusion layer between the anode and the vent forming face of a container which are located in the outermost layer of an electrode group.

[0017]Hereafter, lithium storage bodies, an anode, a negative electrode, a nonaqueous electrolyte contained layer, an air diffusion layer, and a container are explained.

[0018]1) As for lithium storage-bodies lithium storage bodies, it is more desirable than a negative electrode to have a conductive support plate with which the lithium storage reservoir containing the material which emits a lithium ion, and said lithium storage reservoir are supported with **** potential. It is preferred to contact the lithium storage reservoir side to a negative electrode.

[0019]If the lithium storage reservoir which does not have a conductive substrate on this negative electrode is laminated when the negative electrode is arranged in the outermost layer of the electrode group, Since a lithium storage reservoir loses its shape easily when the volume of a lithium storage reservoir decreases with discharge of a lithium ion, there is a possibility that a lithium storage reservoir may exfoliate from a negative electrode. Since a negative electrode can be made to support a lithium storage reservoir with a base material even if the volume of a lithium storage reservoir decreases with discharge of a lithium ion by laminating the lithium storage reservoir made to hold to a conductive substrate to a negative electrode, the exfoliation from the negative electrode of a lithium storage reservoir can be controlled. Since it is arranged inside an electrode group, the lithium storage reservoir can hold a lithium storage reservoir by the electrode or a nonaqueous electrolyte contained layer, and when the outermost layer of an electrode group is [both] anodes, even if there is no conductive substrate, it can control the exfoliation from a negative electrode.

[0020]As a conductive substrate, a nonporous metal plate, the metal plate of porous structure, the board of the net shape which knit the metal wire, etc. can be mentioned, for example. As metal which forms a conductive substrate, copper, stainless steel, nickel, etc. can be mentioned, for example.

[0021]As for the lithium content of a lithium storage reservoir, it is preferred to carry out to 1% of the weight or more.

[0022]When using what contains occlusion and the carbonaceous material to emit for a lithium ion as a negative electrode, as a material which emits a lithium ion with **** potential rather than a negative electrode, a lithium metal, a lithium alloy, etc. can be mentioned, for example. When using a lithium metal oxide as a negative electrode, as a material which emits a lithium ion with **** potential rather than a negative electrode, a lithium metal, a lithium alloy, carbonaceous material, etc. can be mentioned, for example. The kind of material to be used can be made into one kind or two kinds or more.

[0023]As said lithium alloy, a lithium aluminum alloy, a lithium tin alloy, a lithium lead alloy, a lithium silicon base alloy, etc. can be mentioned, for example.

[0024]As said lithium metal oxide, a lithium tin oxidation thing, a lithium silicon oxide, lithium titanium oxide, a lithium niobium oxidation thing, a lithium tungsten oxide, etc. can be mentioned, for example.

[0025]When the material which emits lithium with **** potential rather than a negative electrode is powder, it can mold into a sheet shaped with a binder. As said binder, for example Polytetrafluoroethylene (PTFE), Polyvinylidene fluoride (PVdF), ethylene-propylene-butadiene rubber (EPBR), a styrene butadiene rubber (SBR), carboxymethyl cellulose (CMC), etc. can be used.

[0026]If metallic materials, such as a lithium metal and a lithium alloy, are used as a material which emits lithium with **** potential rather than a negative electrode, since the metallic material can process sheet shape independently, it can form a lithium storage reservoir, without using a binder.

[0027]As for lithium storage bodies, it is desirable to be arranged in the anode in a negative electrode and the field which has not countered. When are arranged in an anode and the field which counters, and the volume of a lithium storage reservoir contracts in connection with a lithium ion moving to a negative electrode from a lithium storage reservoir, a possibility of producing ***** is between a nonaqueous electrolyte contained layer, and an anode and a negative electrode. By arranging a lithium storage reservoir in an anode and the negative-electrode side which has not countered, ***** resulting from the volumetric shrinkage of the lithium storage reservoir accompanying discharge of a lithium ion can be controlled.

[0028]The area of a lithium storage reservoir is the same as that of a negative electrode, or its small thing is preferred. It is because there is a possibility of the portion which a lithium storage reservoir and an anode counter directly arising, and producing a charge-and-discharge reaction between a lithium storage reservoir and an anode when area of a lithium storage reservoir is made larger than negative-electrode area.

[0029]2) **** -- this anode is provided with the following

Positive pole collector.

The positive electrode layer supported by this positive pole collector.

[0030]This anode is produced by the method explained to the following (A) or (B), for example.

[0031](A) Carry out dry blending of carbonaceous material and the binder, and obtain a positive electrode layer by drying after rolling this mixture to film state and producing a film. An anode is obtained by sticking this positive electrode layer to a positive pole collector by pressure.

[0032](B) Apply to a charge collector the slurry obtained by mixing carbonaceous material and a binder in a solvent, and obtain an anode by rolling after drying.

[0033]As carbonaceous material, Ketchen black, acetylene black, carbon black, furnace black, activated

carbon, an activated carbon fiber, and charcoal can be mentioned, for example.

[0034]The particles which have the function to reduce oxygen evolution excess voltage, such as cobalt phthalocyanine, on the surface of carbonaceous material may be made to support. By having such composition, it is possible to raise the efficiency of the reduction reaction of oxygen.

[0035]A binder has the function to maintain the shape of a positive electrode layer and to paste up a positive electrode layer on a charge collector. As this binder, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), ethylene-propylene-butadiene rubber (EPBR), a styrene butadiene rubber (SBR), etc. can be used, for example.

[0036]It is preferred to use porous conductive substrates (a mesh, a punched metal, an expanded metal, etc.) as a positive pole collector, in order to diffuse oxygen promptly. As construction material of said conductive substrate, stainless steel, nickel, aluminum, iron, titanium, etc. can be mentioned, for example. In order that said charge collector may control oxidation, oxidation-resistant metal or alloy may be covered by the surface.

[0037]As for the blending ratio of the carbonaceous material in an anode, and a binder, it is preferred that it is the range of 70 to 98 % of the weight of carbonaceous material and 2 to 30 % of the weight of binders.

[0038]3) **** -- this negative electrode is provided with the following
Negative pole collector.

The negative-electrode-active-material contained layer supported by said negative pole collector.

[0039]As negative electrode active material, the material which carries out occlusion discharge of the lithium ion can be used, for example.

[0040]As a material which carries out occlusion discharge of the lithium ion, the material currently conventionally used for the lithium ion battery or the lithium cell can be used. Especially, it is preferred to use at least one kind of material chosen from the group which consists of carbonaceous material which carries out occlusion discharge of a metallic oxide, metallic sulfide, metal nitride, and the lithium ion as negative electrode active material.

[0041]As carbonaceous material which carries out occlusion discharge of the lithium ion, For example, a graphite material or carbonaceous materials, such as black lead, corks, carbon fiber, and spherical carbon, The graphite material or carbonaceous material obtained by heat-treating at 500-3000 ** to thermosetting resin, an isotropic pitch, a mesophase pitch, mesophase pitch system carbon fiber, a mesophase microsphere, etc. can be mentioned.

[0042]As said metallic oxide, a tin oxidation thing, a silicon oxide, lithium titanium oxide, a niobium oxidation thing, a tungsten oxide, etc. can be mentioned, for example.

[0043]As said metallic sulfide, a tin sulfide, a titanium sulfide, etc. can be mentioned, for example.

[0044]As a negative pole collector, the conductive substrate of porous structure and a nonporous conductive substrate can be used, for example. These conductive substrates can be formed from copper, stainless steel, or nickel, for example. Since especially the conductive substrate of porous structure can make quick the diffusion rate of the lithium ion from a lithium storage reservoir to a negative-electrode-active-material contained layer, it is preferred. After using a mesh, a punched metal, an expanded metal, etc. or making a metallic foil support a negative-electrode-active-material contained layer as a conductive substrate of porous

structure, what opened the hole can be used for said metallic foil as a conductive substrate of porous structure.

[0045]The negative electrode containing negative electrode active material like carbonaceous material applies to a charge collector the suspended solid obtained by kneading negative electrode active material and a binder under existence of a solvent, for example, and after drying, it can produce it by pressing or 2 to 5 times multi stage story pressing once by a desired pressure.

[0046]As said binder, for example Polytetrafluoroethylene (PTFE), Polyvinylidene fluoride (PVdF), ethylene-propylene-butadiene rubber (EPBR), a styrene butadiene rubber (SBR), carboxymethyl cellulose (CMC), etc. can be used.

[0047]As for the blending ratio of said carbonaceous material and said binder, it is preferred that it is the range of 80 to 98 % of the weight of carbonaceous material and 2 to 20 % of the weight of binders.

[0048]4) As a nonaqueous electrolyte contained layer nonaqueous electrolyte contained layer, the separator with which liquefied nonaqueous electrolyte is impregnated, a solid nonaqueous electrolyte layer, etc. can be used, for example.

[0049]Liquefied nonaqueous electrolyte is prepared by dissolving lithium salt in a nonaqueous solvent, for example.

[0050]As a nonaqueous solvent, a publicly known nonaqueous solvent can be used as a solvent of a lithium secondary battery. For example, the 1st solvent that comprises either [at least] propylene carbonate (PC) or ethylene carbonate (EC), It is more preferred than PC and EC to use the nonaqueous solvent which makes a subject a mixed solvent with one or more sorts of nonaqueous solvents (the 2nd solvent is called hereafter) whose donor numbers it is hypoviscosity and are 18 or less.

[0051]As the 2nd solvent, for example Dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), Diethyl carbonate (DEC), methylpropyl carbonate (MPC), isopropanal PIOME chill carbonate, ethyl propionate, methyl propionate, gamma-butyrolactone (gamma-BL), ethyl acetate, methyl acetate, etc. are mentioned. These 2nd solvent can be independent or can be used with the gestalt of two or more sorts of mixtures. Especially, the chain carbonate which includes carbonic ester combination or an ester bond in intramolecular is preferred. As for the boiling point of the 2nd solvent, it is preferred that it is not less than 90 **.

[0052]As for the loadings of said 1st solvent in said mixed solvent, it is preferred that it is 10 to 80% in a volume ratio. The loadings of the 1st more desirable solvent are 20 to 75% in a volume ratio.

[0053]As a desirable presentation of said mixed solvent, gamma-BL, EC and PC, gamma-BL, and DEC can be mentioned. [EC, PC, EC, DEC and EC, PC, DEC and EC, gamma-BL and EC, gamma-BL, DEC and EC, PC,] It is preferred to make the volume ratio of EC into 10 to 80% of within the limits in each mixed solvent. The volume ratio of more desirable EC is 25 to 65% of range.

[0054]As lithium salt, for example Lithium perchlorate (LiClO_4), Lithium hexafluorophosphate (LiPF_6), tetrafluoride lithium borate (LiBF_4), Although lithium trifluoromethanesulfonate (LiCF_3SO_3), screw trifluoromethane sulfonyl amide lithium [$\text{LiN}(\text{CF}_3\text{SO}_2)_2$], etc. are mentioned, it is not limited to these.

[0055]As for the dissolved amount to the nonaqueous solvent of lithium salt, it is desirable to be referred to as 0.5-2.5 mol / L.

[0056]As a separator, the porosity film containing polyethylene, polypropylene, or polyvinylidene fluoride (PVdF), the nonwoven fabric made of a synthetic resin or the nonwoven fabric made from glass fiber, etc. can be used, for example.

[0057]As for the porosity of a separator, it is preferred to use 30 to 90% of range. This is based on the following reasons. When porosity is made less than 30%, there is a possibility that it may become difficult to acquire high electrolysis solution holdout in a separator. On the other hand, when porosity exceeds 90%, there is a possibility that it may become impossible to obtain sufficient separator intensity. The more desirable range of porosity is 35 to 60%.

[0058]As a solid nonaqueous electrolyte layer, the film containing lithium salt and a polymer material can be used, for example. As a polymer material, polyethylene oxide (PEO), polyacrylonitrile (PAN), PVdF, etc. can be mentioned, for example. Having explained in the liquefied nonaqueous electrolyte mentioned above as lithium salt and the same thing can be mentioned.

[0059]In order to raise ion conductivity in solid nonaqueous electrolyte, to it, it is preferred that the organic solvent contains. As this organic solvent, ethylene carbonate (EC), propylene carbonate (PC), gamma-butyrolactone (gamma-BL), the carbonate of fluoride content, and chain carbonate can be mentioned, for example. Said organic solvent may be used combining two or more kinds, although these may be used independently. Such solid nonaqueous electrolyte can improve the ion conductivity of a lithium ion.

[0060]5) As an oxygen diffusion layer of oxygen *****, nonwoven fabrics made of a synthetic resin, such as a porosity film, polypropylene, and PTFE, glass fiber nonwoven fabric, etc. containing fluoro-resins, such as polyethylene, polypropylene, or PTFE, can be mentioned, for example.

[0061]6) The container of ***** can be formed from a metal plate, the sheet which has a resin layer, etc., for example.

[0062]Said metal plate can be formed from iron, stainless steel, and aluminum, for example.

[0063]It is preferred to comprise a metal layer and a resin layer which covers said metal layer as said sheet. As for said metal layer, forming from aluminium foil is preferred. On the other hand, said resin layer can be formed from thermoplastics, such as polyethylene and polypropylene. Said resin layer can be made into a monolayer or multilayer structure.

[0064]Subsequently, P and Q which were mentioned above are explained with reference to drawing 1 - drawing 5.

[0065]Drawing 1 is a top view showing an example (for example, thin nonaqueous electrolyte battery) of the nonaqueous electrolyte battery concerning this invention, Drawing 2 is a sectional view obtained when the container of the nonaqueous electrolyte battery of drawing 1 is cut along an a-b line, Drawing 3 is another sectional view obtained when the container of the nonaqueous electrolyte battery of drawing 1 is cut along an a-b line, and drawing 4, It is a top view showing an example (for example, coin type nonaqueous electrolyte battery) of the nonaqueous electrolyte battery concerning this invention, and drawing 5 is a sectional view obtained when the container of the nonaqueous electrolyte battery of drawing 4 is cut along an a-b line.

[0066]Drawing 1 is an example of the thin nonaqueous electrolyte battery using the bag-shaped container 1 made from a film, and the positive pole terminal 2 and the negative pole terminal 3 have extended from the container 1. Two or more vents 4 are formed in the whole surface of the container 1. In the nonaqueous

electrolyte battery which has the structure shown in this drawing 1, said P expresses the distance of the field 5 in which said vent 4 is formed, this forming face 5, and the field 6 which counters. About said Q, the distance from each vent 4 to the furthest part of the inner surface of the container 1 is measured, and the minimum of the measured distance is set to Q.

[0067]As shown in drawing 3, when the vent 4 is formed in the two fields 7a and 7b where the bag-shaped container 1 counters mutually, it differs from the case where it is drawing 2 which the definition of said P mentioned above. Namely, as for said P, the distance between said two fields 7a and 7b serves as one half of these sizes of 2P by 2P.

[0068]On the other hand, drawing 4 is an example of a coin type nonaqueous electrolyte battery which uses a metal vessel, and this metal vessel is provided with the following.

The metal positive electrode container 8 in which the opening of two or more vents 4 is carried out.
The metal negative-electrode container 10 with which caulking immobilization of this positive electrode container 8 is carried out via the insulating gasket 9.
An electrode group is stored in the space surrounded with the positive electrode container 8 and the negative-electrode container 10.

[0069]In this coin type nonaqueous electrolyte battery, P expresses the distance of the positive electrode container 8 and the negative-electrode container 10 with which the vent 4 is formed. On the other hand, about Q, the distance from each vent 4 to the furthest part of the inner surface of a metal vessel is measured, and the minimum of the measured distance is set to Q.

[0070]Subsequently, an example of the nonaqueous electrolyte battery concerning this invention is explained with reference to drawing 6 - drawing 8.

[0071]Drawing 6 is a sectional view showing an example (for example, thin nonaqueous electrolyte battery) of the nonaqueous electrolyte battery concerning this invention, drawing 7 is a typical top view about the nonaqueous electrolyte battery of drawing 6, and drawing 8 is a typical sectional view obtained when the container of the nonaqueous electrolyte battery of drawing 6 is cut along an a-b line.

[0072]The electrode group 11 is stored in the bag-shaped container 1 made from a film. The electrode group 11 is provided with the following.

For example, the anode 14 which has the structure where the positive electrode layer 13 was supported by the positive pole collector 12 which consists of a porosity conductive substrate.

For example, the negative electrode 17 which has the structure where the negative-electrode-active-material contained layer 16 was supported by the negative pole collector 15 which consists of a porosity conductive substrate.

The nonaqueous electrolyte contained layer 18 arranged between the anode 14 and the negative electrode 17.

[0073]As for the positive pole terminal 2, one end was connected to the positive pole collector 12, and the other end has extended to the exterior of the container 1. On the other hand, as for the negative pole terminal 3, one end was connected to the negative pole collector 15, and the other end has extended to the exterior of the container 1.

[0074]The lithium storage bodies 19 are provided with the following.

The lithium storage reservoir 20 containing the material which emits a lithium ion with **** potential rather than the negative electrode 17.

The conductive substrate 21 with which said lithium storage reservoir 20 is supported.

The lithium storage bodies 19 are laminated by said electrode group 11 so that the lithium storage reservoir 20 may touch the negative pole collector 15. The conductive substrate 21 is electrically connected with the negative pole terminal 3.

[0075]The opening of many vents 4 as a vent is carried out to the anode 14 among the containers 1 in the field which counters. The air diffusion layer 22 as an oxygen diffusion layer is arranged between the field and the positive pole collector 12 in which the vent 4 is formed. The removable sealing tape 23 is stuck on vent 4 forming face of the container 1 so that the vent 4 may be plugged up.

[0076]If the sealing tape 14 is removed, air will be supplied in the container 1 through the vent 4. The supplied air is uniformly diffused in a positive electrode surface by passing the air diffusion layer 22, and the oxygen gas in this air is used as positive active material.

[0077]In the nonaqueous electrolyte battery which has the structure shown in this drawing 4 - drawing 6, the distance R is the distance from the vent 4 to the surface of the lithium storage reservoir 20, and satisfies the following expression of relations (1).

[0078]

$$0.25P \leq R \leq 0.98Q \quad (1)$$

This expression of relations (1) is explained. Although it is necessary to make it open a vent wide by exfoliation of a sealing tape etc. to start use of a nonaqueous electrolyte battery, and to supply oxygen from a vent in a container, at the time of an oxygen supply start, diffusion of lithium from a lithium storage reservoir to a negative-electrode-active-material contained layer may not be completed. If distance R is made smaller than $0.25P$, the distance of lithium storage bodies and a vent becomes near, and since the lithium storage reservoir which remains in a container at the time of an oxygen supply start oxidizes by the oxygen supplied in the container, high service capacity cannot be obtained. On the other hand, since the touch area of lithium storage bodies and a negative electrode will become small if the distance R becomes larger than $0.98Q$, it becomes difficult to supply lithium of sufficient quantity for a negative electrode from lithium storage bodies, and high service capacity cannot be obtained.

[0079]The effect of explaining to the following (a) - (c) can be acquired by making distance R into more than $0.25P$ and below $0.98Q$.

[0080](a) Since the air diffusion layer by which compression storage was carried out in connection with this volumetric shrinkage until now expands although the volumetric shrinkage of lithium storage bodies arises when lithium is spread from lithium storage bodies to the negative-electrode-active-material contained layer, it is avoidable that a crevice arises in an electrode group.

[0081](b) Lithium of sufficient quantity for a negative electrode can be supplied from lithium storage bodies.

[0082](c) It can suppress that the lithium storage reservoir which remains in a container at the time of the beginning of using oxidizes by the oxygen incorporated from the vent in the container.

[0083]These (a) The service capacity of a nonaqueous electrolyte battery can be improved as a result of - (c).

[0084]Although the air lithium cell was mentioned as an example of the nonaqueous electrolyte battery

concerning this invention in the above explanation, it is possible to apply the metal ion which consists of sodium, aluminum, magnesium, caesium, etc. as negative electrode active material to other air metal cells which use occlusion and the material which can be emitted. In other air metal cells, it is good as an electrolyte to use metal salt, such as sodium, aluminum, magnesium, and caesium.

[0085]

[Example] Hereafter, with reference to the drawing which mentioned the example of this invention above, it explains in detail.

[0086] (Example 1)

90 % of the weight of <production of anode> Ketchen black (EC600JDTM), and after carrying out dry blending of 10 % of the weight of the polytetrafluoroethylenes, in length, width obtained the positive electrode layer of 200-micrometer-thick film state by 28 mm at 40 mm by rolling. This positive electrode layer was stuck to the mesh made from titanium which is a positive pole collector by pressure, and the anode was obtained. The end of the positive pole terminal was connected to the portion which the positive pole collector of the obtained anode exposed.

[0087] Copper foil which is a charge collector was made to apply and dry 97 % of the weight of <production of negative electrode> mesophase pitch carbon fiber, and the slurry obtained by carrying out the wet blending of 3 % of the weight of the polyvinylidene fluorides in N-methyl pyrrolidone. Subsequently, in length, width produced the negative electrode of 200-micrometer-thick film state by 28 mm at 40 mm by carrying out the opening of the hole 1 mm in diameter to a charge collector at a rate of 1-5 1 cm² hits. The end of the negative pole terminal was connected to the portion which the negative pole collector has exposed among the obtained negative electrodes.

[0088] In 38 mm, <production of lithium storage bodies> length was [width] 26 mm, length stuck 100-micrometer-thick metal lithium foil to the 100-micrometer-thick mesh made from nickel by pressure by 26 mm at 38 mm, and width produced lithium storage bodies. The lead was welded to the portion exposed from the peripheral part of a lithium storage reservoir among the mesh made from nickel, and this lead was further connected to the negative pole collector exposed portion of a negative electrode.

[0089] Liquefied nonaqueous electrolyte was prepared by doing 1.0 mol / L dissolution of lithium perchlorate (LiClO₄) into the nonaqueous solvent which mixed <preparation of liquefied nonaqueous electrolyte> ethylene carbonate 50 volume %, and propylene carbonate 50 volume %.

[0090] The 400-micrometer-thick porosity film [nonwoven fabric / 500-micrometer-thick / made from glass fiber] made from PTFE as an air diffusion layer again was prepared as a <cell assembly> separator. The laminate film of composition of having covered both sides of aluminium foil with the resin layer was processed into saccate, and the eight-piece opening of the vent 0.8 mm in diameter was carried out to one side.

[0091] Lithium storage bodies, the negative electrode, the separator, the anode, and the air diffusion layer were laminated one by one, the lithium storage reservoir of lithium storage bodies was contacted to the negative pole collector in this case, and laminated material was obtained as an electrode group. This laminated material was stored so that an air diffusion layer might counter with a vent forming face in the bag made from a laminate film. Subsequently, the sealing tape was stuck on the vent forming face, and the vent was blockaded.

The tip of the positive pole terminal and the negative pole terminal was made to extend from the opening of laminate film bag manufacture.

[0092]After pouring in liquefied nonaqueous electrolyte from an opening in a bag, the nonaqueous electrolyte secondary battery which has the structure shown in drawing 4 mentioned above - drawing 6 was manufactured by thermal melting arrival's processing the opening of a saccate laminate film, and obturating it.

[0093]When the section vertical to the vent forming face of the container of the obtained cell was observed using the transmission-X-ray device and the distance P, Q, and R was measured, the result explained below was obtained.

[0094]It was 1.5 mm when the distance R from a vent to the lithium storage reservoir surface was measured about arbitrary vents among eight vents. The minimum of 5.3 mm of the eight distance acquired from the vent by measuring the distance to the furthest part of a container internal surface about each of eight vents was set to Q. Distance of 1.8 mm of the field in which the vent in a container is formed, this forming face, and the field which counters was set to P.

[0095]It was 0.45 when $0.25P$ was computed from the obtained value. $0.98Q$ was 5.19. Therefore, the distance R has satisfied the expression of relations (1) mentioned above.

[0096](Examples 2-4) The nonaqueous electrolyte secondary battery was manufactured like Example 1 mentioned above except changing the distance P, Q, and R, as shown in the following table 1 by changing the thickness of an air diffusion layer and a separator, and the position of an air vent.

[0097](Example 5) Except using the lithium storage bodies explained below, it manufactured, as Example 1 mentioned above explained, and the nonaqueous electrolyte secondary battery which has the structure shown in drawing 9 and drawing 10 was obtained.

[0098]Length the 100-micrometer-thick metal lithium foil [<production of lithium storage bodies> length / in 38 mm / width] 24 (lithium storage reservoir) at 26 mm at 38 mm. At 26 mm, it was stuck to the 100-micrometer-thick mesh 25 made from nickel by pressure, the vent carried out the opening of the hole 26 3 mm in diameter to the position arranged in the upper part further at the time of a cell assembly, and width obtained lithium storage bodies.

[0099]When the section vertical to the vent forming face of the container of the obtained cell was observed using the transmission-X-ray device and the distance P, Q, and R was measured, the result explained below was obtained.

[0100]It was 1.4 mm when the distance R from the vent 4 to the lithium storage reservoir 24 surface was measured about the arbitrary vents 4 among the eight vents 4. the eight vents 4 -- the minimum of 5.0 mm of the eight distance acquired from the vent 4 by measuring the distance to the furthest part of the inner surface of the container 1 about each was set to Q. Distance of 1.3 mm of the field 5 in which the vent 4 in the container 1 is formed, this forming face 5, and the field 6 which counters was set to P.

[0101]It was 0.33 when $0.25P$ was computed from the obtained value. $0.98Q$ was 4.90. Therefore, the distance R has satisfied the expression of relations (1) mentioned above.

[0102](Comparative example 1) Except storing an electrode group in a container so that the lithium storage-bodies side of an electrode group may counter with a vent, it manufactured like Example 1 mentioned above, and the nonaqueous electrolyte secondary battery of the structure shown in drawing 11 and drawing 12 was

obtained.

[0103]It was 0.3 mm when the distance R from the vent 4 to the lithium storage reservoir 20 surface was measured about the arbitrary vents 4 among the eight vents 4. Such a distance R has not satisfied the expression of relations (1) mentioned above.

[0104](Comparative example 2) Except using the lithium storage bodies explained below, it manufactured, as Example 1 mentioned above explained, and the nonaqueous electrolyte secondary battery which has the structure shown in drawing 13 and drawing 14 was obtained.

[0105]At 40 mm, width stuck the lithium foil 28 only to the end of the mesh 27 made from nickel which is 28 mm by pressure, and <production of lithium storage bodies> length obtained lithium storage bodies.

[0106]It was 5.2 mm when the distance R from the vent 4 to the lithium storage reservoir 28 surface was measured about the arbitrary vents 4 among the eight vents 4. Such a distance R has not satisfied the expression of relations (1) mentioned above.

[0107]It was neglected at 20 ** for 24 hours after assembling the nonaqueous electrolyte secondary battery of Examples 1-5 and the comparative examples 1-2 which were acquired. Subsequently, after removing a sealing tape from a nonaqueous electrolyte secondary battery and discharging to 2.0V by 0.4 mA of discharge current, the charge-and-discharge cycle test charged to 4.0V by 0.2 mA of charging current is carried out at 20 **, the service capacity of 1 cycle eye and 20 cycle eye is measured, and the result is shown in the following table 1.

[0108]

[Table 1]

	距離R (mm)	0. 2 5 P (mm)	0. 9 8 Q (mm)	1ヶ月目放電容量 (mA h)	20ヶ月目放電容量 (mA h)
実施例 1	1. 5	0. 4 5	5. 1 9	2 1 6	2 0 6
実施例 2	1. 5	1. 2 5	5. 1 9	2 1 5	2 0 2
実施例 3	0. 7	0. 2 5	5. 0 0	2 2 1	2 1 1
実施例 4	1. 5	0. 4 5	1. 6 5	2 0 4	1 9 4
実施例 5	1. 4	0. 3 3	4. 9	2 1 0	2 0 0
比較例 1	0. 3	0. 4 5	5. 1 9	8 4	1 5
比較例 2	5. 2	0. 4 5	5. 1 9	5	< 1

[0109]It turns out that the rechargeable battery of Examples 1-5 is excellent in the both sides of initial capacity and cycle performance compared with the rechargeable battery of the comparative examples 1-2 so that clearly from Table 1.

[0110]When the cell of Example 1 was again charged after the end of a charge-and-discharge cycle test, it decomposed and the powder X diffraction analyzed the negative-electrode center section and the end, in lithium and carbon, also in any of a negative-electrode center section and an end, the lithium ion had intercalated at a rate of 1:6.2.

[0111]On the other hand, when the cell of the comparative example 1 was disassembled after the end of a charge-and-discharge cycle test, air bubbles were formed between the separator and the negative electrode. When the cell of the comparative example 2 was disassembled after the end of a charge-and-discharge cycle test and the powder X diffraction analyzed the carbon material of the anode, most intercalation of the lithium

ion to carbon was not observed.

[0112](Example 6) Except using the negative electrode explained below and lithium storage bodies, it manufactured like Example 1 mentioned above, and the nonaqueous electrolyte secondary battery which has the structure shown in drawing 15 was obtained.

[0113]By making the copper mesh which is a charge collector apply and dry 97 % of the weight of <production of negative electrode> mesophase pitch carbon fiber, and the slurry obtained by carrying out the wet blending of 3 % of the weight of the polyvinylidene fluorides in N-methyl pyrrolidone, The negative-electrode-active-material contained layer 31 was made to hold to both sides of the charge collector 30, and, in length, width produced the negative electrode 32 of 200-micrometer-thick film state [in 28 mm] at 40 mm. The end of the negative pole terminal 3 was connected to the portion which the negative pole collector has exposed among the obtained negative electrodes.

[0114]In <production of lithium storage bodies> length, at 38 mm, width prepared 200-micrometer-thick metal lithium foil as the lithium storage reservoir 33 by 26 mm.

[0115]The same air diffusion layer as Example 1 which was <-cell-assembled, > was mentioned above explained, an anode, liquefied nonaqueous electrolyte, and a separator were prepared. The laminate film processed into saccate was prepared and the opening of the vent which is eight pieces 0.8 mm in diameter was carried out to both sides, respectively.

[0116]The air diffusion layer 22, the anode 14, the separator 18, the negative electrode 32 (the negative-electrode-active-material contained layer 31, the negative pole collector 30), The lithium storage reservoir 33, the negative electrode 32 (the negative pole collector 30, the negative-electrode-active-material contained layer 31), the separator 18, the anode 14, and the air diffusion layer 22 were laminated one by one, and as Example 1 which mentioned this laminated material above explained, it stored in the bag made from a laminate film. Subsequently, the sealing tape was stuck on both sides of the bag-shaped container, respectively, and the vent was blockaded. The tip of the positive pole terminal and the negative pole terminal was made to extend from the opening of laminate film bag manufacture.

[0117]As Example 1 explained from the opening in a bag, after pouring in liquefied nonaqueous electrolyte, the nonaqueous electrolyte secondary battery which has the structure shown in drawing 15 was manufactured by thermal melting arrival's processing the opening of a saccate laminate film, and obturating it.

[0118]When the section vertical to the vent forming face of the container of the obtained cell was observed using the transmission-X-ray device and the distance P, Q, and R was measured, the result explained below was obtained.

[0119]It was 1.5 mm when the distance R from the vent 4 to the lithium storage reservoir 33 surface was measured about the arbitrary vents 4 among the 16 vents 4. the 16 vents 4 -- about each, the distance from the vent 4 to the furthest part of the inner surface of the container 1 was measured, and the minimum of 5.3 mm of 16 kinds of measured distance was set to Q. 1.8 mm which is 1/2 which is the distance of 3.6 mm of two fields in which the vent in the container 1 is formed was set to P.

[0120]It was 0.45 when 0.25P was computed from the obtained value. 0.98Q was 5.19. Therefore, the distance R had satisfied the expression of relations (1) mentioned above.

[0121](Examples 7-8) The nonaqueous electrolyte secondary battery was manufactured like Example 6

mentioned above except changing the distance P, Q, and R, as shown in the following table 1 by changing the thickness of an air diffusion layer and a separator, and the position of an air vent.

[0122](Comparative example 3) Two electrode groups which have the structure shown in drawing 6 mentioned above were prepared, it piled up so that the lithium storage bodies 19 might be located in the outermost layer, and the lamination type electrode group was obtained. Except storing such an electrode group in a container, the nonaqueous electrolyte secondary battery was obtained like Example 6 mentioned above. That is, in this cell, the field in which the vent 4 of the container 1 is formed, and the lithium storage bodies 19 have countered.

[0123]It was 0.3 mm when the distance R from a vent to the lithium storage reservoir 20 surface was measured about arbitrary vents among 16 vents. Such a distance R has not satisfied the expression of relations (1) mentioned above.

[0124](Comparative example 4) Except using the lithium storage bodies explained below, as Example 6 mentioned above explained, the nonaqueous electrolyte secondary battery was obtained.

[0125]At 40 mm, width stuck lithium foil only to the end which is a mesh made from nickel which is 28 mm by pressure, and <production of lithium storage bodies> length obtained lithium storage bodies.

[0126]It was 5.2 mm when the distance R from a vent to the lithium storage reservoir surface was measured about arbitrary vents among 16 vents. Such a distance R has not satisfied the expression of relations (1) mentioned above.

[0127]It was neglected at 20 ** for 24 hours after assembling the nonaqueous electrolyte secondary battery of Examples 6-8 and the comparative examples 3-4 which were acquired. Subsequently, after removing a sealing tape from a nonaqueous electrolyte secondary battery and discharging to 2.0V by 0.4 mA of discharge current, the charge-and-discharge cycle test charged to 4.0V by 0.2 mA of charging current is carried out at 20 **, the service capacity of 1 cycle eye and 20 cycle eye is measured, and the result is shown in the following table 2.

[0128]

[Table 2]

	距離R (mm)	0. 2 5 P (mm)	0. 9 8 Q (mm)	1サイクル放電容量 (mA h)	20サイクル放電容量 (mA h)
実施例6	1. 5	0. 4 5	5. 1 9	4 3 0	4 0 8
実施例7	1. 5	1. 2 5	5. 1 9	4 1 5	3 9 5
実施例8	1. 5	0. 4 5	1. 6 5	4 2 0	4 0 0
比較例3	0. 3	0. 4 5	5. 1 9	1 5 0	3 5
比較例4	5. 2	0. 4 5	5. 1 9	2 0	2

[0129]It turns out that the rechargeable battery of Examples 6-8 is excellent in the both sides of initial capacity and cycle performance compared with the rechargeable battery of the comparative examples 3-4 so that clearly from Table 2.

[0130]

[Effect of the Invention]As explained in full detail above, according to this invention, the nonaqueous electrolyte battery whose service capacity improved can be provided.

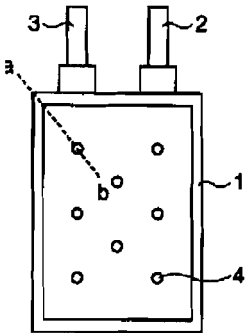
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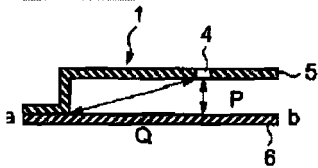
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DRAWINGS

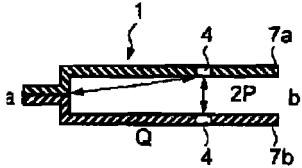
[Drawing 1]



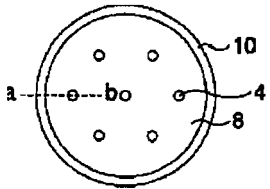
[Drawing 2]



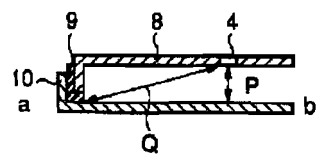
[Drawing 3]



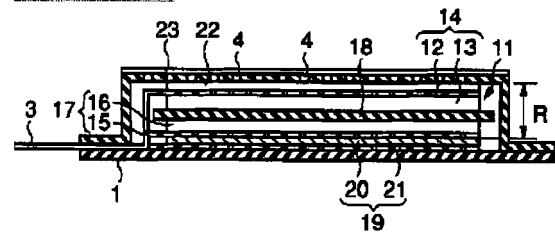
[Drawing 4]



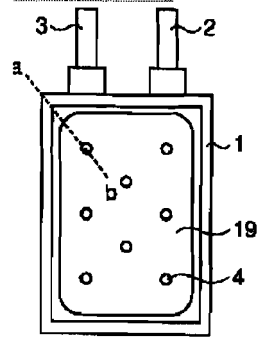
[Drawing 5]



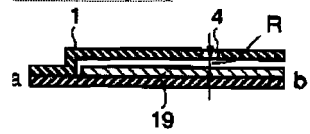
[Drawing 6]



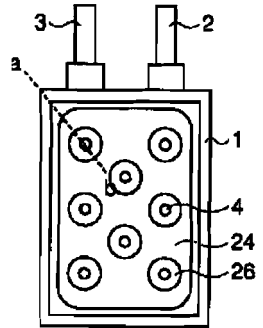
[Drawing 7]



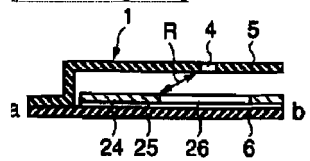
[Drawing 8]



[Drawing 9]



[Drawing 10]



[Drawing 11]

